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Study of the LLE, VLE and VLLE of the ternary system water + 1-butanol + isoamyl alcohol at 101.3 kPa

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Abstract

In this work it has been determined experimentally the liquid-liquid equilibrium of the water + 1-butanol + isoamyl alcohol system at 303.15K and 313.15K. The UNIQUAC, NRTL and UNIFAC models have been employed to correlate and predict LLE and compare them with the experimental data. Additionally, the vapor-liquid and vapor-liquid-liquid equilibria of this system have also been determined using a modified Fischer labodest still. The data obtained have been used to correlate and obtain the binary interaction parameters for UNIQUAC and NRTL. It has been analysed the validity of the models to reproduce the VLE and VLLE data.

1. Introduction

The search for sustainable alternative fuels destined for use in industry has, in general, been on the rise due to the growing concerns regarding: the future availability of oil reserves; environmental problems (global warming and climate change) [1]; increasing crude oil prices; the volatility of oil supply; and existing legislation that restricts the use of non-renewable energy sources and mandates the use of fuel from renewable sources [2]. Several non-petroleum based liquid biofuels obtained from biomass may constitute viable alternatives. In this regard, alcohols such as methanol, ethanol and butanol are competitive due to their advantageous physico-chemical properties.

Ethanol is the most widely used biofuel today, but it suffers from several disadvantages that suggest it needs to be replaced. The most important disadvantage is that ethanol produces only about three-quarters of the energy obtained from conventional gasoline [3]. Butanol is seen as a potential alternative to ethanol because it is less volatile and explosive, has a higher flash point, and lower vapour pressure, which makes it safer to handle. It contains more energy, it is less hygroscopic and can easily mix with gasoline in any proportion. In addition, butanol and gasoline have a similar air to fuel ratio and energy content. Butanol can be used directly or blended with gasoline or diesel without any vehicle retrofit and supplied through existing gasoline pipelines [4].

These second-generation biofuels are made from the inedible parts of lignocellulosic biomass. The biobutanol production process involves pre-treatment and hydrolysis of raw material followed by fermentation of sugars to butanol. The principal obstacle is the high production cost which includes: the capital investment and the cost of equipment, raw materials, pre-treatment, the enzyme, strain development, recovery, as well as the cost of R&D, sales and marketing of butanol. Nowadays, numerous research groups are working on the cost contributing factors while also analysing the R&D strategies and the latest technologies that will render the process practical and cost-effective [5].

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Biofuel purification is an important step in the overall production process as it involves the separation of biobutanol from the undesirable impurities, water in particular. During the production of biobutanol by fermentation, or obtained through reaction with bioethanol as a feed, several other by-products appear as impurities (such as pentanols) [6]. Our research group has been investigating the viability of using hydrocarbons as entrainers in the dehydration of butanol [7, 8, 9]. Going further into the research of obtaining a biofuel for use as an additive in conventional fuel, it is necessary to not only separate the 1-butanol from the water, but also to separate it from the other impurities present in the reaction media. This, in turn, requires obtaining experimental data for the liquid-liquid, vapour-liquid and vapour-liquid-liquid equilibria (LLE, VLE, and VLLE, respectively) of these ternary systems. One of the impurities is isoamyl alcohol.

In the present work, we report experimental VLE and VLLE data for the water + 1-butanol + isoamyl alcohol ternary system at a constant pressure of 101.3 kPa, as well as LLE data at different temperatures (303.15 and 313.15 K) and the same pressure. We also discuss the accuracy with which the activity coefficient models can predict these various equilibria. Only LLE data for this system have been published previously in the literature [14].

Water + 1-butanol + isoamyl alcohol is a type 2 heterogeneous ternary system with two partially miscible pairs: water + 1-butanol and water + isoamyl alcohol. It has two binary heterogeneous azeotropes, water + 1-butanol and water + isoamyl alcohol [10].

2. Experimental

2.1 Chemicals

Specifications for all chemical compounds used in the experiments are provided in Table 1. Ethanol (used as internal standard), 1-butanol and isoamyl alcohol were used as supplied by the provider without further purification. Ultrapure water was obtained using a Mili-Q Plus system. The Karl-Fisher titration method was used to determine the water content of the chemicals.

Table 1. *Chemicals employed in this work.*

Chemical	Provider	Initial purity (mass fraction)	water content (mass fraction)	Purification method	Analysis method
1-butanol	Merck	>0.995	≤0.001	None	GC[a]
Isoamyl alcohol	Merck	>0.990	≤0.002	None	GC[a]
Ethanol	Merck	>0.999	<0.001	None	GC[a]

[a] GC, Gas Chromatography

2.2 Experimental procedure

2.2.1 LLE data determination

Mixtures of known overall composition belonging to the heterogeneous region were prepared in glass tubes and sealed with screw caps and Teflon septum. These tubes were submerged partially inside a thermostatic bath maintained at a constant and controlled temperature. They were also shaken vigorously to speed up equilibration. Afterwards, the tubes were left in the bath at the same temperature in order to permit decantation and promote phase separation. The bath temperature was 303.15 K in one of the experiments and 313.15K in the other.

After the phase separation, weighed samples were extracted from both layers by means of syringes and injected into vials. A measured amount of ethanol was added in each of the vials as an internal standard for quantification purposes and to avoid phase splitting when the samples began to cool down outside of the thermostatic bath. An additional sample was taken from each of the organic layers and their water content was checked against the Karl Fischer technique. The Water content determined by the Karl Fischer titration is used to verify the value obtained from the chromatography.

Each of the vials were analysed by gas chromatography. The organic phases were analysed in a Shimadzu GC14 with a Porapak Q packed column and a thermal conductivity detector (TCD). The oven temperature was set to 463 K, the injector to 483 K, and the TCD to 483 K. The current was fixed at 100 mA. The carrier gas, helium, was supplied at a flow rate of 30 mL/min.

The aqueous phases were analysed by means of an Agilent 7820A chromatograph. In both GC systems the same chromatographic phase (Porapak Q) was used. A TCD and a Flame Ionisation Detector (FID) were placed in series just after the column. The helium flow rate was 20 mL/min. The temperatures were 503, 523, 523 and 523 K for the oven, injector, TCD and FID. This chromatograph has been employed In order to analyze the composition of the organic compounds in the aqueous phase whose concentrations are low. It possesses not only a TCD but it also has a FID. The FID being a more sensitive detector, it allows a better quantification of the organic compounds.

In order to quantify the samples' composition, standards of a known composition, and with ethanol as internal standard, were prepared and analysed by the same procedure used on the samples.

2.2.2 VLLE and VLE data determination

The VLE and VLLE data have been measured by means of a modified Fischer Labodest unit with an ultrasonic probe fitted inside its boiling chamber. The use of ultrasound to obtain equilibrium data when heterogeneous liquid mixtures are present has been studied and shown in a previous paper [11] to be adequate for the intended purpose. The experimental procedure is described in a previous work [7].

A liquid mixture (homogeneous or heterogeneous) is brought to the boiling point. The resulting vapour carries some of the liquid phases through the Cotrell pump. After the Cotrell pump the liquid phases and their equilibrium vapour are separated in a chamber: the liquid phases exit this chamber through a conduit and returns to the

mixing chamber. The vapour goes to a condenser where it is condensed and, subsequently, is also returned to the mixing chamber. Just before the condenser an amount of the vapour is bypassed through a heated tube (to avoid condensation) by means of a peristaltic pump. This tube carries the vapour to the chromatograph where a 6-way valve injects some of it into the chromatograph injector of the Shimadzu GC14A. This chromatograph is connected with the distillation equipment in order to analyze the vapor composition on line (to avoid vapor condensation and its phase splitting). This vapour is analysed under the same conditions as the organic phases during the LLE determination. The sample containing the equilibrium liquid can be extracted by means of an electrovalve that lifts the glass rod which seals the tube that, in turn, returns liquid to just before the mixing chamber. Temperatures of the vapour are recorded during the course of the experiment using a Pt-100 with an accuracy of 0.006K according to its certificate of calibration (SCALE ITS90) [12]. The pressure is measured and controlled at 101.3 kPa using a High-Speed Pneumatic Pressure Controller Model CPC3000 by Mensor.

If the collected liquid sample is heterogeneous, it is treated the same way as in the LLE determination except that the temperature in the thermostatic bath is now set to the boiling point of the collected liquid.

3. Results

3.1 Liquid-liquid equilibrium data.

The experimental data obtained are presented in Tables 2 and 3. The binary liquid-liquid equilibrium of water + 1-butanol is reported in a previous work [13].

***Table 2**. Experimental LLE data for the system water + 1-butanol + isoamyl alcohol at 303.15K and at 101.3 kPa. Compositions are reported in units of mole fraction. The relative standard uncertainty in composition is $u_r(x)=u(x)/x= 4\%$ and the standard uncertainty in T is u (T) = 0.1 K and in P is u (P) =2 kPa.*

Organic phase			Aqueous phase		
x_{water}	$x_{1\text{-butanol}}$	$x_{isoamyl}$	x_{water}	$x_{1\text{-butanol}}$	$x_{isoamyl}$
0.504[13]	0.496[13]	0.000[13]	0.983[13]	0.017[13]	0.000[13]
0.458	0.494	0.049	0.984	0.015	0.001
0.417	0.481	0.103	0.986	0.013	0.001
0.404	0.436	0.159	0.987	0.011	0.002
0.400	0.385	0.216	0.989	0.010	0.002
0.358	0.347	0.295	0.990	0.008	0.003
0.352	0.285	0.363	0.990	0.006	0.003
0.344	0.219	0.437	0.991	0.005	0.004
0.341	0.149	0.510	0.992	0.003	0.004
0.311	0.078	0.611	0.994	0.001	0.004

0.299	0.000	0.701	0.995	0.000	0.005

***Table 3**. Experimental LLE data for the system water + 1-butanol + isoamyl alcohol at 313.15K. Compositions are reported in units of mole fraction. The relative standard uncertainty in composition is $u_r(x)=u(x)/x=4\%$ and the standard uncertainty in T is u (T) = 0.1 K and in P is u (P) =2 kPa.*

Organic phase			Aqueous phase		
x_{water}	$x_{1\text{-butanol}}$	$x_{isoamyl}$	x_{water}	$x_{1\text{-butanol}}$	$x_{isoamyl}$
0.516[13]	0.484[13]	0.000[13]	0.981[13]	0.019[13]	0.000[13]
0.469	0.484	0.047	0.986	0.014	0.000
0.439	0.460	0.101	0.987	0.012	0.001
0.416	0.426	0.158	0.988	0.010	0.002
0.398	0.382	0.220	0.989	0.009	0.002
0.393	0.329	0.278	0.990	0.007	0.002
0.406	0.260	0.333	0.991	0.006	0.003
0.370	0.210	0.421	0.991	0.005	0.003
0.336	0.149	0.515	0.992	0.003	0.004
0.320	0.079	0.602	0.994	0.001	0.004
0.308	0.000	0.692	0.995	0.000	0.005

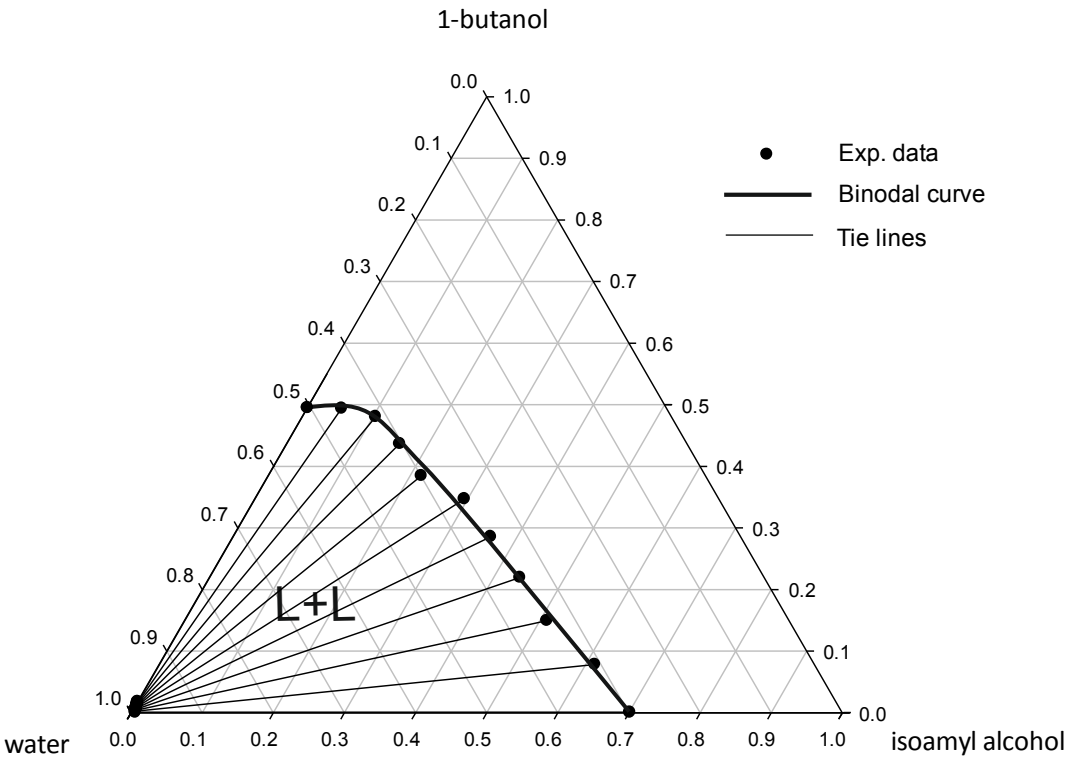

Figure 1. *LLE tie lines at 303.15 K for the system water + 1-butanol + isoamyl alcohol. Compositions reported in units of mole fraction.*

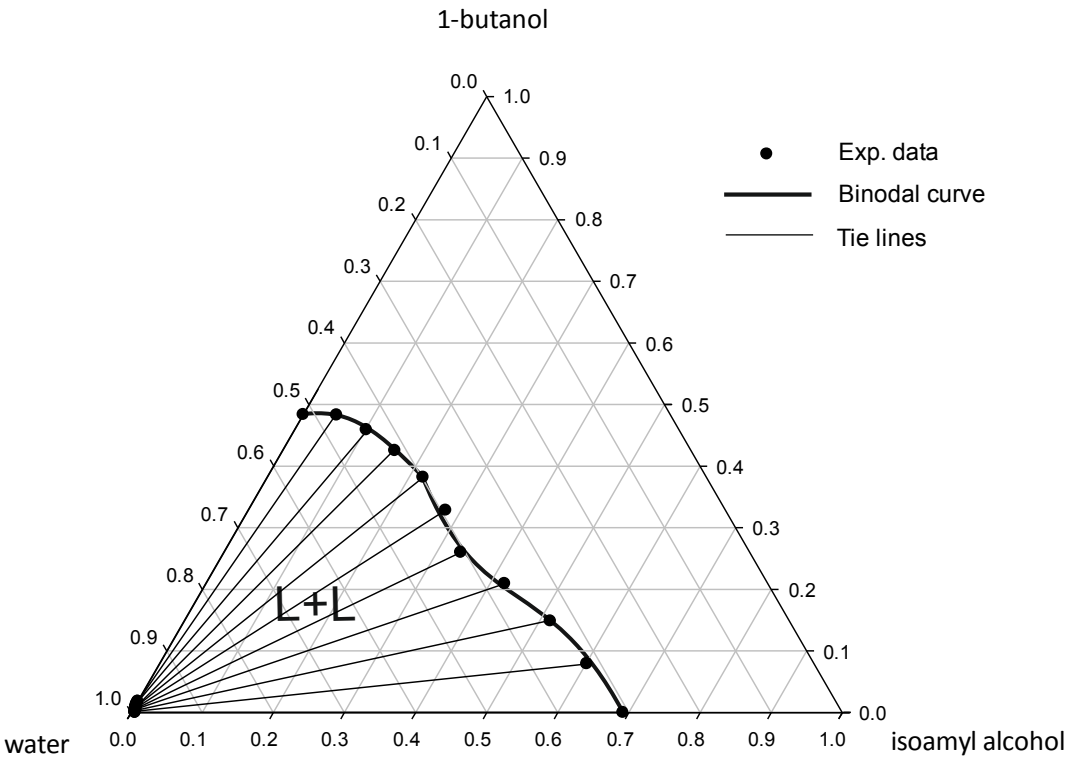

Figure 2*. LLE tie lines at 313.15 K for the system water + 1-butanol + isoamyl alcohol. Compositions reported in units of mole fraction.*

The data in Tables 2 and 3 are plotted in Figs. 1 and 2. Figure 3 is a plot of LLE data at 298.15, 333.15 and 368.15 K, obtained by Zhu et al. [14]. On the one hand, the LLE does not seem very sensitive to the temperature in going from 303.15 to 313.15 K, or in the organic phases, from 298.15 to 368.15 K, as reported by Zhu et al. On the other hand, the results presented by Zhu et al. differ greatly from the ones determined experimentally. Moreover, the LLE data obtained in Ref. [14] for the water + 1-butanol pair do not match any of the other references found in the literature [15].

In contrast, we have determined the LLE for the binary pair water + isoamyl alcohol at 303.15, 313.15 K and at the boiling temperature (around 369 K) (see Table 2, 3 and 4). Several authors have determined this binary LLE at various temperatures (See Refs. [16 – 20]). In Figure 4 we plot these LLE equilibria. It is evident that our experimental points coincide with the other authors' to within uncertainty. The LLE of water + isoamyl alcohol in the temperature range considered tends to be slightly less heterogeneous when the temperature is raised.

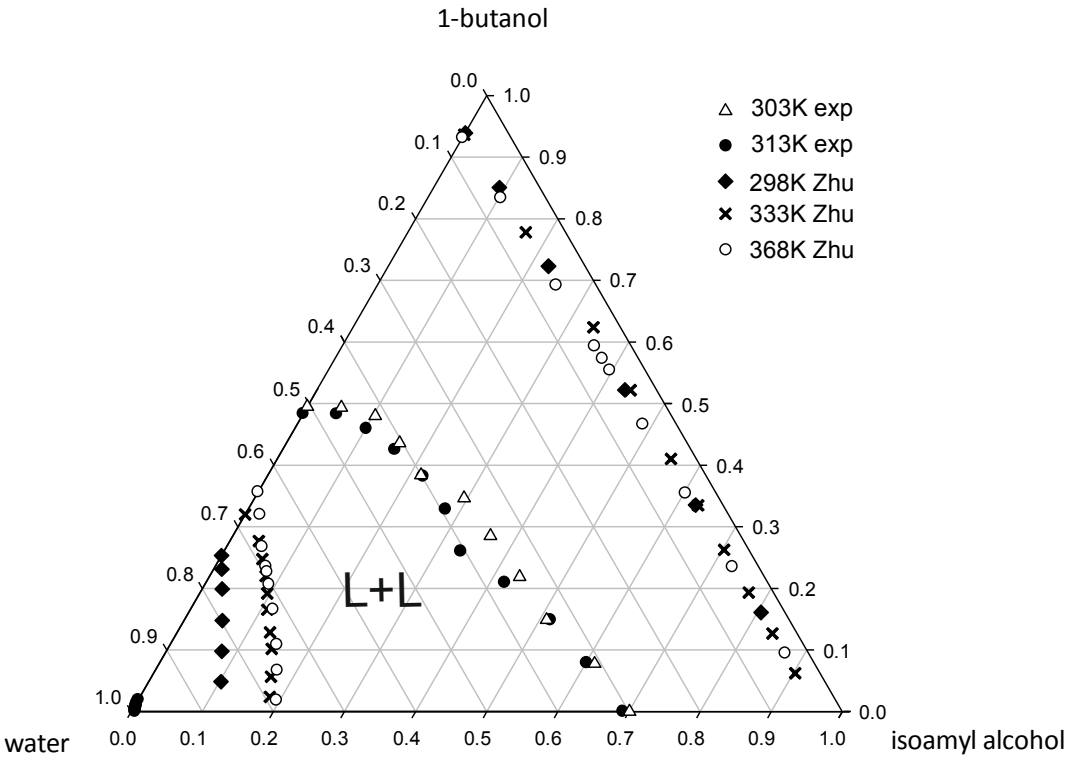

***Figure 3**. LLE experimental data of water + 1-butanol + isoamyl alcohol at 303.15 and 313.15 K. Data obtained by Zhu et al. [14] at 298, 333 and 368 K are also shown. Compositions reported in units of mole fraction.*

***Figure 4**. Binary LLE for the pair water + isoamyl alcohol at different temperatures and comparison with literature. The composition is reported in percentage by weight of isoamyl alcohol.*

3.2 Vapor-liquid and vapor-liquid-liquid equilibrium data

Table 4 collects the VLLE data obtained at 101.3 kPa, and Table 5, the VLE data of the homogeneous liquids in the system.

The thermodynamic L/W Wisniak consistency point-to-point test [21] has been used to check the thermodynamic consistency of the experimental data. The value of the L/W are found within the 0.96 to 1.00 range as can be checked in the supplementary data. This value range shows that the experimental vapor-liquid and vapor-liquid-liquid data are indeed consistent.

***Table 4**. VLLE data of water + 1-butanol + isoamyl alcohol at 101.3 kPa. Compositions are reported in units of mole fraction. The relative standard uncertainty in composition is $u_r(x)=u(x)/x=4\%$ and the standard uncertainty in T is u (T) = 0.06 K and in P is u (P) =0.1 kPa.*

	Organic Phase			Aqueous Phase			Vapour		
T/K	x_{water}	$x_{1\text{-butanol}}$	$x_{isoamyl}$	x_{water}	$x_{1\text{-butanol}}$	$x_{isoamyl}$	y_{water}	$y_{1\text{-butanol}}$	$y_{isoamyl}$
365.73[11]	0.638[11]	0.362[11]	0.000[11]	0.979[11]	0.021[11]	0.000[11]	0.754[11]	0.246[11]	0.000[11]
365.93	0.596	0.380	0.024	0.985	0.015	0.000	0.757	0.233	0.011
365.92	0.546	0.391	0.063	0.986	0.013	0.001	0.778	0.200	0.021
366.16	0.525	0.371	0.104	0.987	0.012	0.002	0.769	0.196	0.035
366.37	0.499	0.331	0.170	0.988	0.009	0.003	0.776	0.168	0.056
366.60	0.487	0.279	0.233	0.989	0.008	0.003	0.777	0.143	0.079
366.92	0.480	0.194	0.326	0.992	0.005	0.004	0.787	0.101	0.111
366.98	0.488	0.171	0.342	0.992	0.004	0.004	0.789	0.093	0.118
367.12	0.478	0.153	0.369	0.993	0.003	0.004	0.789	0.080	0.131
367.24	0.462	0.141	0.397	0.993	0.003	0.004	0.793	0.072	0.135
367.34	0.444	0.126	0.430	0.993	0.003	0.004	0.793	0.063	0.144
367.62	0.431	0.067	0.503	0.994	0.001	0.005	0.797	0.034	0.169
368.06	0.446	0.000	0.554	0.995	0.000	0.005	0.808	0.000	0.192

***Table 5**. VLE data of water + 1-butanol + isoamyl alcohol at 101.3 kPa. Compositions are reported in units of mole fraction. The relative standard uncertainty in composition is $u_r(x)=u(x)/x=4\%$ and the standard uncertainty in T is u (T) = 0.06 K and in P is u (P) =0.1 kPa.*

T/K	x_{water}	$x_{1\text{-butanol}}$	$x_{isoamyl}$	y_{water}	$y_{1\text{-butanol}}$	$y_{isoamyl}$
365.90	0.350	0.610	0.040	0.757	0.234	0.009
365.97	0.322	0.620	0.058	0.739	0.247	0.013
366.18	0.375	0.598	0.028	0.751	0.243	0.006
366.24	0.340	0.355	0.305	0.783	0.145	0.072
366.40	0.350	0.379	0.271	0.780	0.155	0.065
366.42	0.327	0.427	0.246	0.773	0.171	0.056
366.43	0.280	0.643	0.077	0.737	0.249	0.014
366.69	0.302	0.479	0.219	0.764	0.188	0.048
366.86	0.281	0.533	0.187	0.765	0.201	0.035
366.92	0.314	0.341	0.346	0.786	0.137	0.077
367.09	0.285	0.328	0.387	0.785	0.130	0.085
367.22	0.248	0.315	0.437	0.786	0.123	0.091
368.41	0.278	0.674	0.048	0.746	0.246	0.008
368.42	0.246	0.597	0.157	0.734	0.236	0.030
368.44	0.197	0.145	0.658	0.784	0.064	0.152
368.52	0.446	0.521	0.032	0.761	0.230	0.009
368.60	0.182	0.193	0.625	0.790	0.081	0.129
368.86	0.492	0.480	0.028	0.759	0.232	0.009
369.11	0.230	0.237	0.532	0.790	0.096	0.114
369.37	0.175	0.288	0.537	0.782	0.113	0.105
370.69	0.262	0.671	0.067	0.722	0.263	0.014
371.59	0.246	0.604	0.149	0.721	0.245	0.034
372.90	0.220	0.517	0.263	0.717	0.218	0.066
374.97	0.188	0.437	0.376	0.707	0.194	0.098
376.20	0.172	0.378	0.450	0.697	0.177	0.126
376.74	0.167	0.297	0.537	0.713	0.141	0.146
377.95	0.154	0.211	0.635	0.709	0.105	0.186
378.45	0.144	0.324	0.532	0.661	0.169	0.170
379.55	0.109	0.665	0.227	0.548	0.376	0.076
379.77	0.106	0.740	0.154	0.527	0.424	0.049
380.19	0.106	0.586	0.308	0.546	0.346	0.108
380.57	0.106	0.506	0.388	0.568	0.297	0.135
381.23	0.119	0.262	0.619	0.628	0.152	0.220
381.38	0.086	0.794	0.120	0.460	0.497	0.043
381.67	0.105	0.411	0.484	0.577	0.249	0.174
382.40	0.111	0.156	0.734	0.619	0.095	0.286
382.70	0.108	0.284	0.608	0.578	0.183	0.239
383.61	0.065	0.843	0.091	0.379	0.585	0.035

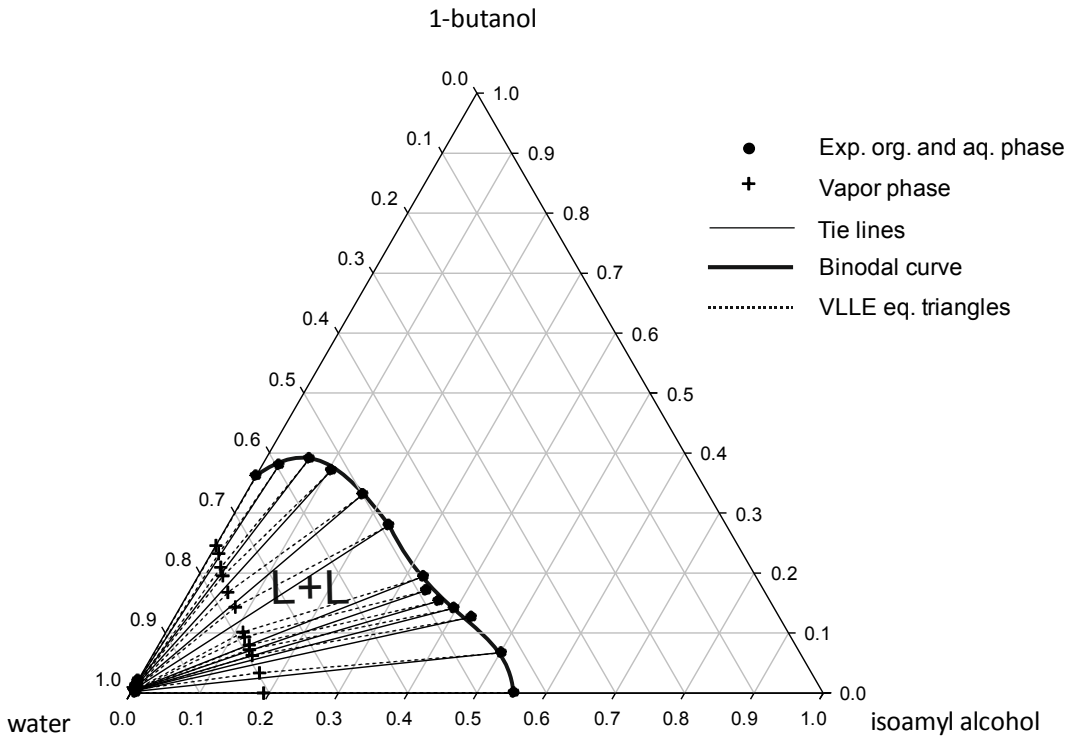

***Figure 5**. VLLE data of water + 1-butanol + isoamyl alcohol at 101.3 kPa. Compositions reported in units of mole fraction.*

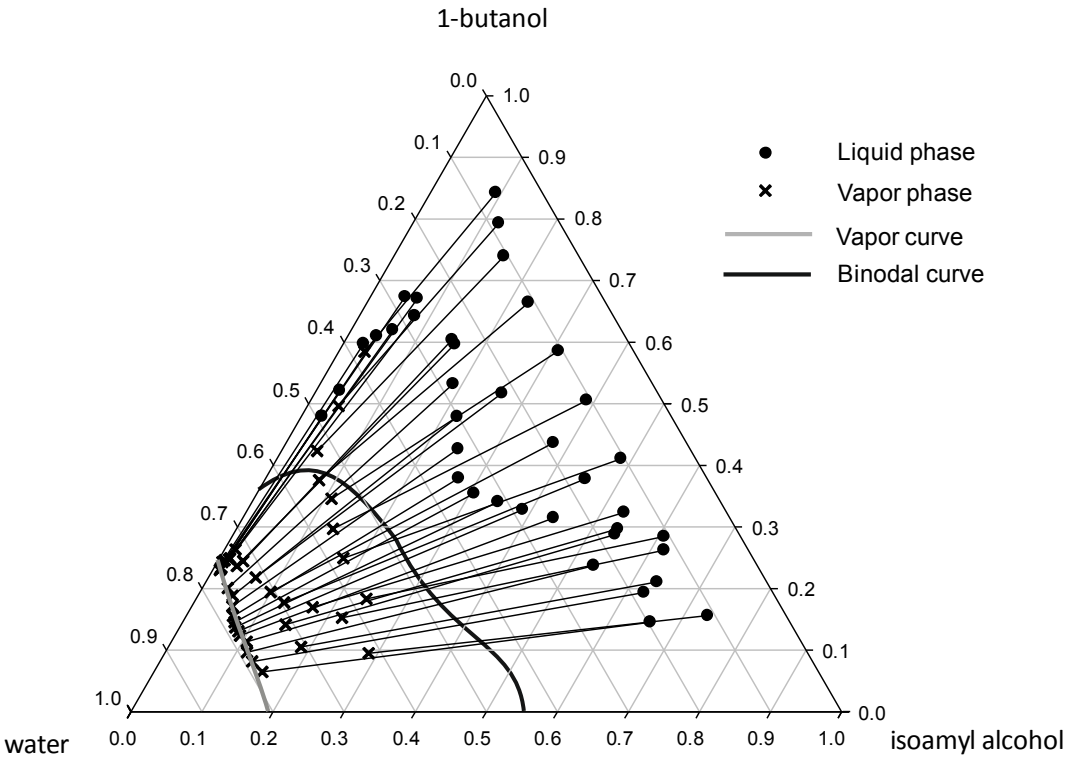

***Figure 6**. VLE data of water + 1-butanol + isoamyl alcohol at 101.3 kPa. Compositions reported in units of mole fraction.*

Figure 5 is a plot of the data in Table 4. This table contains two binary heterogeneous azeotropes: water+1-butanol and water+ isoamyl alcohol. The data corresponding to the water + 1-butanol azeotrope are reported in a previous work [11]. The experimental heterogeneous binary azeotrope of water + isoamyl alcohol in Table 4 has been reported by several authors [10]. The data for this azeotrope range from 368.25 to 368.35K, and the compositions from 0.810 to 0.828 in mole fraction of water. Our compositions are in agreement with the other authors' to within uncertainty. Nevertheless, the temperature that we obtain is slightly lower than that reported in the literature. Based on the VLLE data, it is not possible to ensure the existence of a ternary azeotrope in this system. To the best of our knowledge, its existence has not been reported in the literature either. The vapour phases on the vapour curve are all richer in water and butanol than their equilibrium liquid counterparts, i.e., the vapour vertex of the equilibrium triangles always points towards the water + 1-butanol side of the composition triangle.

Figure 6 shows the VLE data of the liquid phases belonging to the homogeneous region (see Table 5). The heterogeneous phase border is also shown. With the exception of a few points, the liquid phases have an equilibrium vapour that belongs to the heterogeneous region. Moreover, the vapour phase of a large fraction of the homogeneous liquid phases lies on the vapour curve, or occurs within a small range of compositions from it.

4. Data Correlation.

The UNIQUAC and NRTL equations have been used to correlate our experimental data, while, for purposes of prediction and comparison, we have used UNIFAC. The experimental data have been correlated in two different ways: on the one hand, with the isothermal LLE data and, on the other, with the isobaric VLE data. The objective functions of these correlations are the same as those employed in a previous paper [13].

4.1 LLE correlation

The experimental isothermal LLE data for the ternary system have been correlated at two different temperatures by means of the above models. The α parameter in the NRTL model has been kept constant at 0.2. This value is generally recommended by Dechema for water+ alcohols pair in LLE. The correlation of experimental data was carried out separately at each temperature. The binary interaction parameters (BIPs) calculated at 303.15 K are reported in Table 6, and those calculated at 313.15 K, in Table 7.

***Table 6**. Parameters and mean deviations from the LLE correlation at 303K for water (1) + 1-butanol (2) + isoamyl alcohol (3). Bij (K): binary interaction parameters from the NRTL model. Uij-Uii (K): binary interaction parameters from UNIQUAC. Mean deviations (D) of water and 1-butanol in the organic (1) and aqueous phase (2).*

i	j	B_{ij} (K)	B_{ji} (K)	α	U_{ij}-U_{jj} (K)	U_{ji}-U_{ii} (K)
1	2	1495.364	-283.9353	0.2	307.9099	-21.54459
1	3	1625.294	-97.21615	0.2	374.7232	53.22150
2	3	-317.2166	186.2358	0.2	256.8050	-274.9637

Mean Deviation	D x_{11}	D x_{21}	D x_{31}	D x_{12}	D x_{22}	D x_{32}
NRTL	0.013	0.008	0.005	0.002	0.001	0.0003
UNIQUAC	0.007	0.004	0.003	0.004	0.003	0.002

***Table 7**. Parameters and mean deviations from the LLE correlation at 313K for water (1) + 1-butanol (2) + isoamyl alcohol (3). Bij (K): binary interaction parameters from the NRTL model. Uij-Uii (K): binary interaction parameters from UNIQUAC. Mean deviations (D) of water and 1-butanol in the organic (1) and aqueous phase (2).*

i	j	B_{ij} (K)	B_{ji} (K)	α	U_{ij}-U_{jj} (K)	U_{ji}-U_{ii} (K)
1	2	1482.049	-299.0967	0.2	257.9664	11.49461
1	3	1453.324	-91.64391	0.2	253.8073	113.76920
2	3	595.8065	-920.9486	0.2	317.6709	-284.3363

Mean Deviation	D x_{11}	D x_{21}	D x_{31}	D x_{12}	D x_{22}	D x_{32}
NRTL	0.008	0.004	0.004	0.004	0.003	0.003
UNIQUAC	0.010	0.006	0.013	0.002	0.001	0.001

Figures 7 and 8 compare the experimental data and the binodal curves calculated by the UNIQUAC and NRTL models, and predicted by the UNIFAC model.

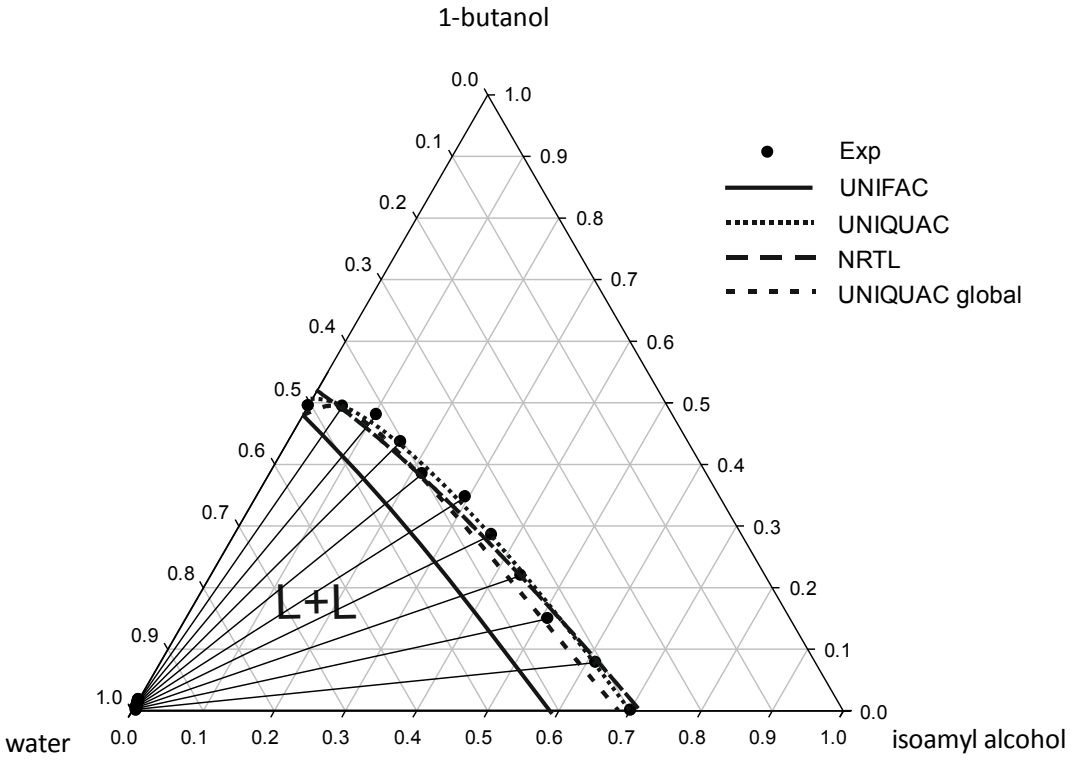

***Figure 7**. LLE data for the system water + 1-butanol + isoamyl alcohol at 303.15 K and binodal curves calculated with UNIQUAC, NRTL and UNIFAC. Compositions are in mole fraction. Parameter from Table 6.*

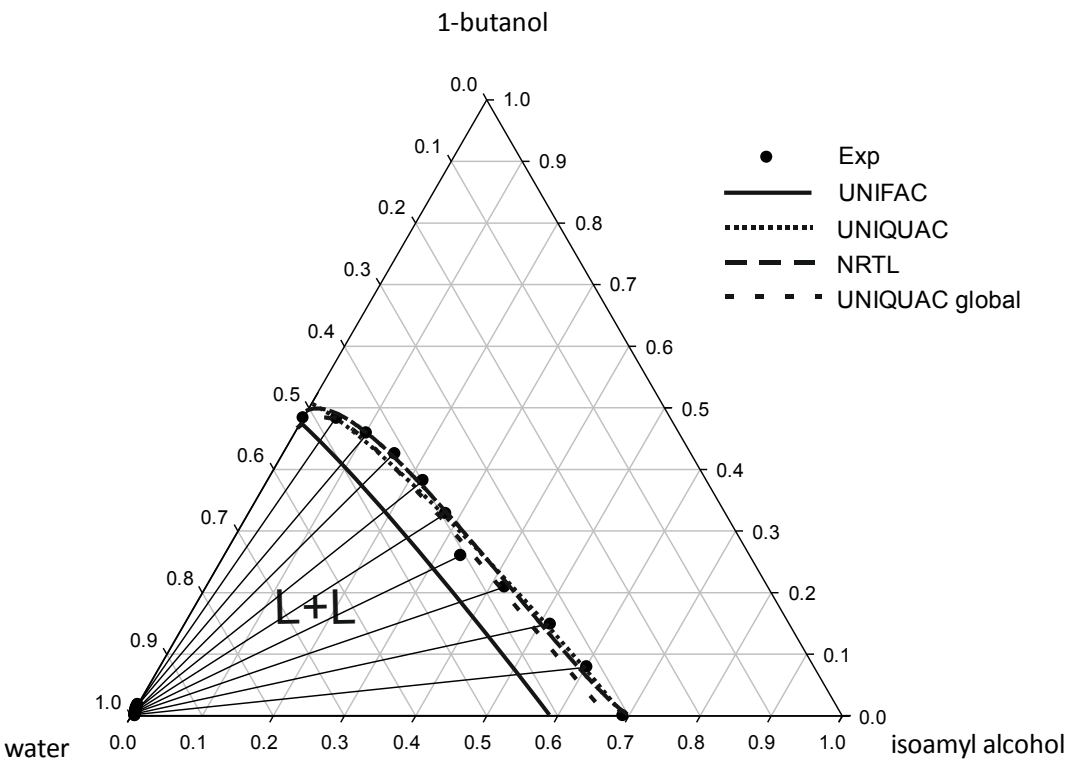

***Figure 8**. LLE data for the system water + 1-butanol + isoamyl alcohol at 313.15 K and binodal curves calculated with UNIQUAC, NRTL and UNIFAC. Compositions are in mole fraction. Parameters from Table 7.*

As can be seen in Figs. 7 and 8, the UNIFAC model predicts a heterogeneous region that is significantly smaller than the experimental one, especially for the water + isoamyl alcohol pair (the error is 10%). In contrast, the UNIQUAC model reproduces the experimental data quite accurately.

4.2 VLLE correlation

The 38 VLE experimental points from the homogeneous region, the 13 ternary VLLE points obtained (treated as 26 VLE points), together with binary data from the bibliography [15], have been correlated using the UNIQUAC and NRTL models. The objective function tries to minimize the sum of the squares of the differences between y_i calculated and y_i experimental (vapor composition) for each i component for each of the experimental liquid phases. Each data of VLLE correspond to two VLE data in the correlation. The alpha value for NRTL model was regressed in the liquid-vapor correlation to try to improve the regression results.

The fitted UNIQUAC and NRTL BIPs for this system are collected in Table 8.

***Table 8**. Parameters and mean deviations from the VLE correlation at 101.3 kPa for water (1) + 1-butanol (2) + isoamyl alcohol (3). Bij (K): binary interaction parameters from the NRTL model.*

Uij-Uii (K): binary interaction parameters from UNIQUAC. Mean deviations (D) of temperature (T) and water (1) and 1-butanol (2) in the vapour phase.

i	J	B_{ij} (K)	B_{ji} (K)	α	$U_{ij}-U_{jj}$ (K)	$U_{ji}-U_{ii}$ (K)
water	1-butanol	1468.34	215.427	0.3634	52.86	258.57
water	isoamyl alcohol	1615.87	361.475	0.3985	224.85	201.33
1-butanol	isoamyl alcohol	-35.5314	35.6741	0.3045	154.35	-171.59

Mean Deviation		D T	D y_1	D y_2	D y_3
	NRTL	1.45	0.0290	0.0195	0.0117
	UNIQUAC	1.13	0.0241	0.0229	0.0070

The mean absolute deviations between experimental and calculated vapour phase mole fractions and temperatures are not very high, and, as a result, the vapour-liquid equilibria are predicted reasonably well. The UNIFAC model also predicts the binodal curve relatively well, except near the water + 1-butanol axis where the model is not able to reproduce the experimental shape. In contrast, the parameters obtained from NRTL and UNIQUAC cannot reproduce the non-isothermal binodal curve accurately, as can be seen in Fig. 9. For this reason, the LLE correlation of the 13 ternary heterogeneous tie-lines (each at a different temperature) has been performed by means of the UNIQUAC model (see Table 9).

***Table 9**. Parameters and mean deviations from the LLE correlation at boiling temperatures for water (1) + 1-butanol (2) + isoamyl alcohol (3). Uij-Uii (K): binary interaction parameters from UNIQUAC. Mean deviations (D) of water and 1-butanol in the organic (1) and aqueous phase (2).*

	I	J	$U_{ij}-U_{jj}$ (K)	$U_{ji}-U_{ii}$ (K)		
	1	2	353.84	-73.53		
	1	3	556.32	-74.02		
	2	3	210.85	-233.11		
Mean Deviation	D x_{11}	D x_{21}	D x_{31}	D x_{12}	D x_{22}	D x_{32}
	0.010	0.005	0.006	0.004	0.003	0.002

In the latter case, the heterogeneous region can be predicted with enough accuracy, as illustrated in Fig. 9, which also shows the organic phase of the binodal curve, plotted with the parameters from Table 9. Nevertheless, neither the equilibrium vapour composition nor temperature are well reproduced. In fact, the residue curve map calculated from these binary interaction parameters (see Fig. 10) predicts a binary azeotrope for the 1-butanol + isoamyl alcohol pair as well as a ternary azeotrope that does not exist.

Additionally a global LLE correlation, using all the experimental LLE data (303.13 K, 313.15 K and at boiling temperature) as input data and UNIQUAC as model. The parameters from this correlation are given in Table 10. The mean deviations obtained are higher than with the other parameter set. The organic phases calculated with this parameter set have been included in Fig 7, 8 and 9. The binodal region calculated with Table 10 parameters is similar to the experimental one for 303.15 and

313K and at boiling temperature. The vapor curve calculated with these parameters is the farthest from the experimental one.

***Table 10**. Parameters and mean deviations from the LLE correlation at all the studied temperatures for water (1) + 1-butanol (2) + isoamyl alcohol (3). Uij-Uii (K): binary interaction parameters from UNIQUAC. Mean deviations (D) of water and 1-butanol in the organic (1) and aqueous phase (2).*

	I	J	U_{ij}-U_{jj} (K)	U_{ji}-U_{ii} (K)		
	1	2	178.42	53.67		
	1	3	171.78	156.06		
	2	3	415.08	-415.58		
Mean Deviation	D x_{11}	D x_{21}	D x_{31}	D x_{12}	D x_{22}	D x_{32}
	0.041	0.030	0.030	0.0068	0.0055	0.0045

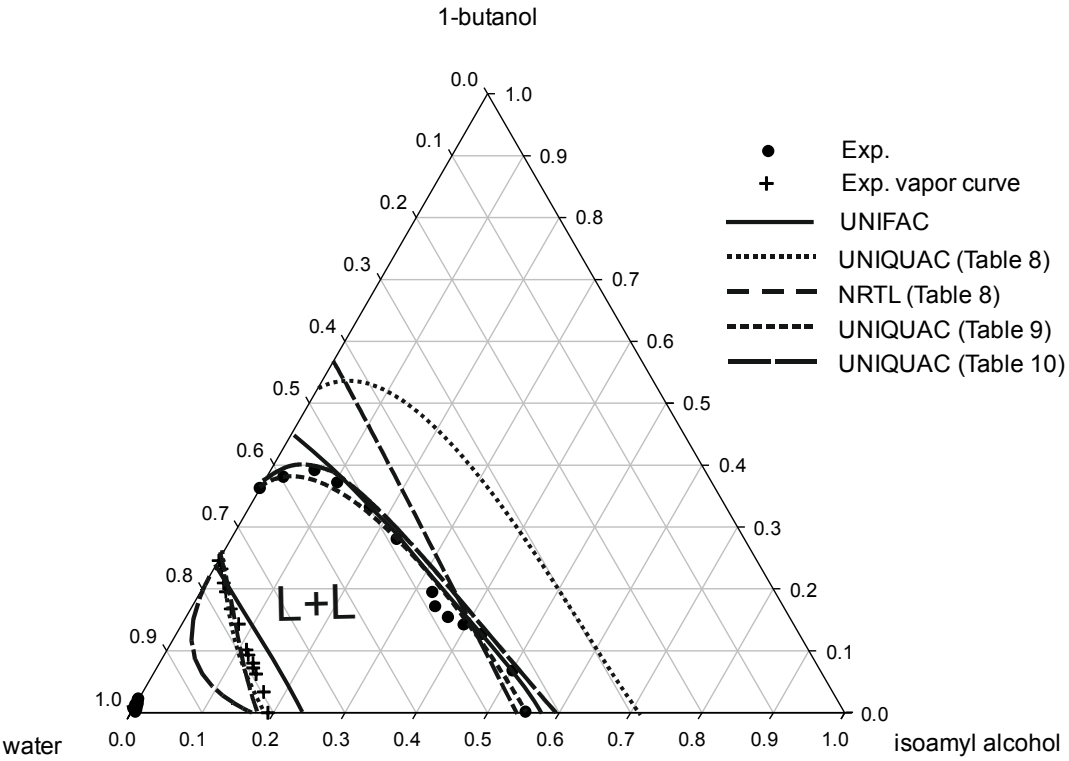

***Figure 9.** Correlation of vapour-liquid-liquid equilibrium data for the system water (1) + 1-butanol (2) + isoamyl alcohol (3) at 101.3 kPa. Heterogeneous region and vapour curve.*

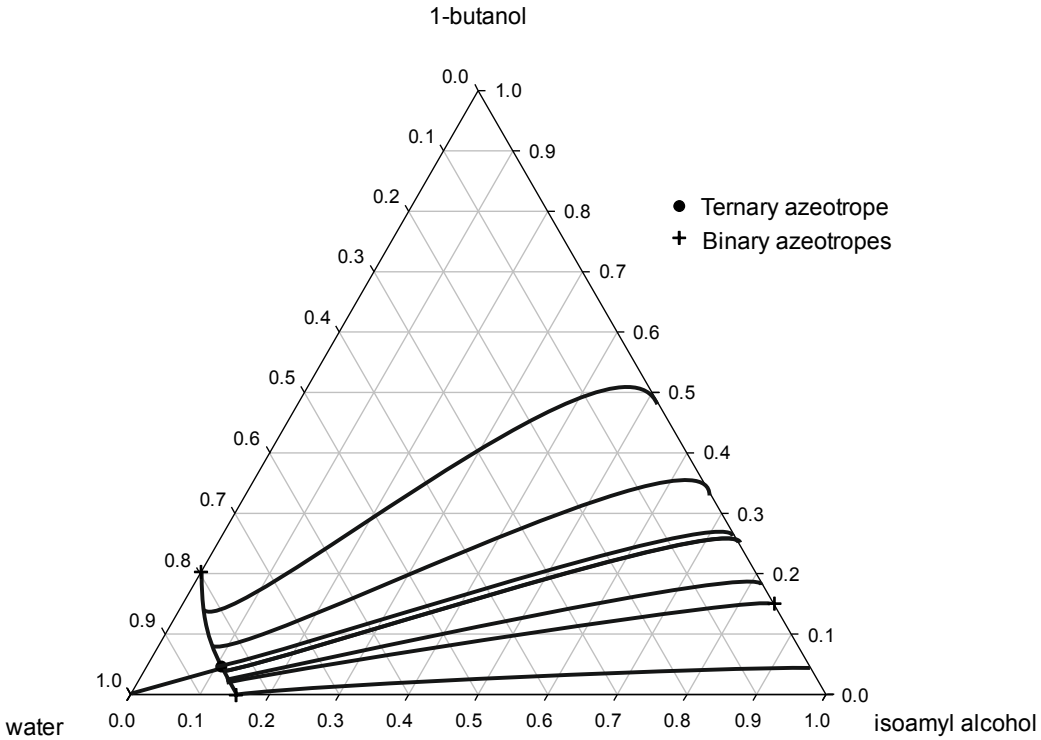

***Figure 10**. Residue curve map at 101.3 kPa, calculated via the UNIQUAC model with the parameters from Table 9.*

In addition to verifying how the models perform in calculating the heterogeneous region, it is convenient to verify how accurately they and their corresponding parameters reproduce the vapor that is in equilibrium with a liquid phase in this system. The K value of 1-butanol (y but/x but) has been calculated for each of the liquid phases in tables 4 and 5. From each model, a vapor composition can be calculated that corresponds to an experimental liquid phase. With the calculated vapor, the calculated K value can be obtained (one in each model). In this way, the error between the experimental K value for 1-butanol and the calculated K value for 1-butanol has been calculated. Figure 11 shows the error in K value in each model as a function of the composition of butanol in the experimental liquid phase. As can be seen, none of the models shows an error in K value that is less than 5% for the whole composition range. That means that none of the models can accurately calculate the butanol content in the vapor phase.

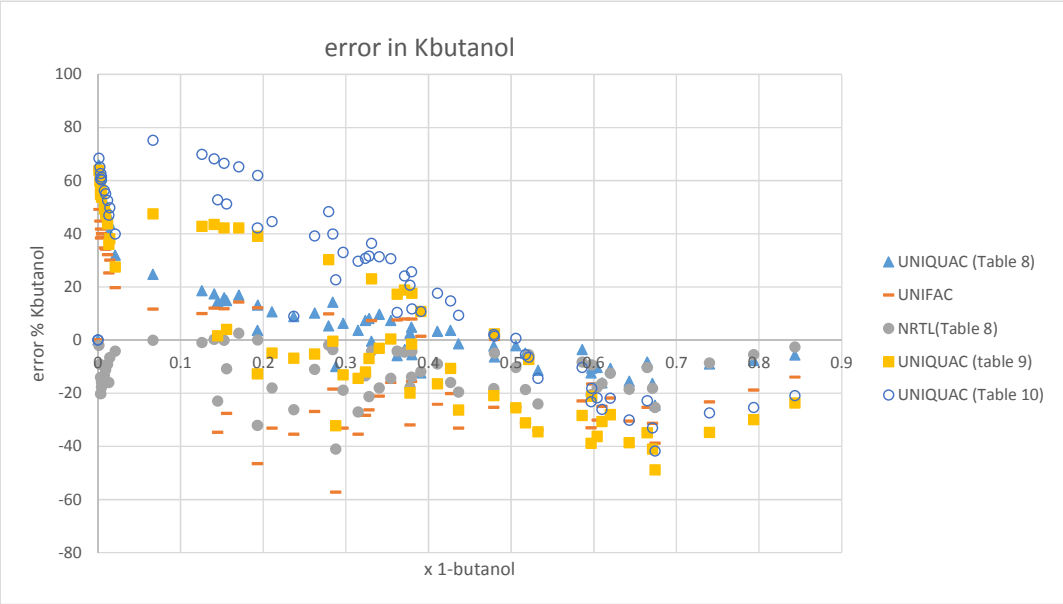

Figure 11. % error in K values of 1-butanol in function of the liquid composition (mole fraction) in 1-butanol between experimental data and calculated with the thermodynamic models studied

Moreover, as can be deduced from figure 11, the parameters in table 8 for the NRTL model generally give errors in K values that are lower than the rest of the models. It can also be seen that the parameters in table 9 for UNIQUAC give a larger error for the vapors than the UNIQUAC parameters in table 8, as mentioned earlier. The UNIQUAC parameters from the global LLE correlation in table 10 are the parameters that reproduce the worse the K value.

5. Conclusions

The liquid-liquid, vapour-liquid and vapour-liquid-liquid equilibria of the system water + 1-butanol + isoamyl alcohol at 101.3 kPa, have been determined at 303.15 and 313.15K for the LLE, and at the boiling temperature for the VLE and VLLE. These data show that this system is little affected by temperature within the studied range for the LLE. The VLLE data do not reveal the existence of a ternary heterogeneous azeotrope.

The VLE of the majority of the studied homogeneous mixtures involve an equilibrium vapour that belongs to the heterogeneous region. In addition, many of the determined vapour points lie near the vapour curve.

The NRTL and UNIQUAC thermodynamic models adequately reproduce the LLE whereas the UNIFAC model predicts a smaller heterogeneous region.

In contrast, these models could not simultaneously, or adequately, reproduce the binodal curve at the boiling temperature and the vapour curve.

Regarding the use of butanol as a biofuel, the equilibrium data presented in this paper show that it could be possible to do a separation of the water from the alcohols via azeotropic distillation and liquid-liquid extraction. Nevertheless an economic study of these processes should be done in order to assess the viability of this butanol separation step.

Supporting Information

"Associated Content: [Results of Wisniak consistency Test, Antoine constants and normal boiling points, Properties of pure compounds used, experimental data used as imput, . Internally calculated activity coefficients, Wisniak L-W point-to-point consistency test values]

Acknowledgement

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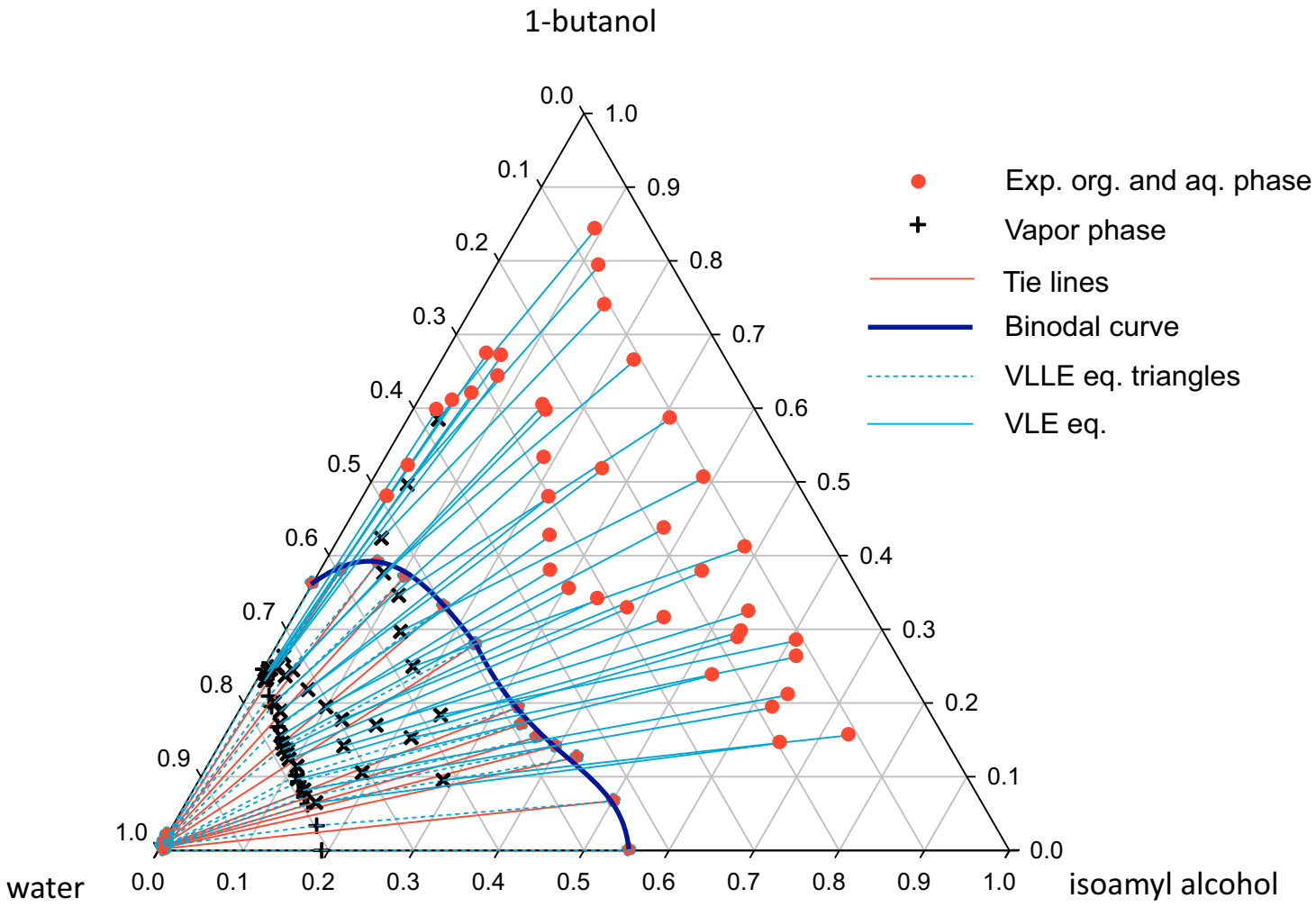
1-butanol
water
isoamyl alcohol
Exp. org. and aq. phase
Vapor phase
Tie lines
Binodal curve
VLLE eq. triangles
VLE eq.